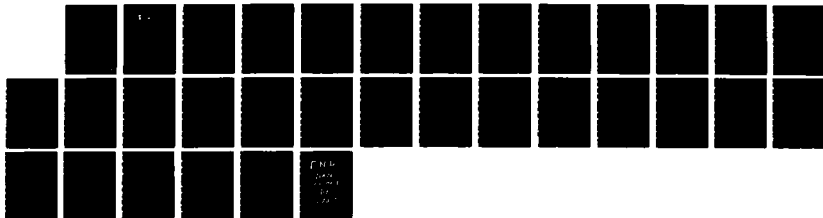AD-A186 277   PYRAZOLE DERIVATIVES OF DIBORANE(4)(U) KENTUCKY UNIV   1/1
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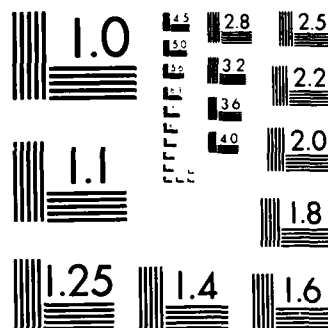   UK/DC/TR-17 N00014-85-K-0611

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Tetrakis(dimethylamino)diborane(4), $(Me_2N)_2B-B(NMe_2)_2$, reacts with four molar equivalents of pyrazole (= Hpz) to form the corresponding species $(pz)_2B-B(pz)_2$ as a dimer with a unique triply bridged pyrazabole structure but in mixture with polymeric product of the same elemental composition; and with excess of Hpz to form the adduct tetrakis(1-pyrazolyl)diborane(4)-bis(pyrazole), $(pz)_2B-B(pz)_2\cdot 2Hpz$. This latter compound crystallizes in the triclinic system in space group $P\bar{1}$ (#2) with $\underline{a}$ = 13.945(2) Å, $\underline{b}$ = 18.392(3) Å, $\underline{c}$ = 9.048(2) Å, α = 109.92(2)°, β = 94.85(1)°, γ = 105.18(1)°, Z = 4 at 296(2) K. The salt $K_2[(pz)_3B-B(pz)_3]$ is obtained on reaction of $(Me_2N)_2B-B(NMe_2)_2$ with two equivalents of Kpz and excess Hpz. This potassium salt reacts with π-allyl-palladium chloride dimers (allyl = CH_2CHCH_2 or $CH_2CCH_3CH_2$) to give $(\eta^3\text{-allyl})Pd(\mu\text{-}pz)_2(pz)B-B(pz)(\mu\text{-}pz)_2Pd(\eta^3\text{-allyl})$ complexes, thus establishing the $[(pz)_3B-B(pz)_3]^{2-}$ ion as a novel bis-polydentate ligand. In solution the $Pd(\mu\text{-}pz)_2B(pz)$ moieties are fluxional and only one set of ^1H NMR signals is observed for the pz groups, even at low temperatures. The formulation involving two bridging and one

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monoclinic system either in space group P2/c (#13) or Pc (#7) with $\underline{a}$ = 18.864(4) A, $\underline{b}$
9.925(3) A, $\underline{c}$ = 16.626(4) A, $\underline{\beta}$ = 115.11(2)$^\circ$, and Z = 4 at 296(2) K.

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C. P. Brock, M. K. Das, R. P. Minton, and K. Niedenzu

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Pyrazole Derivatives of Diborane(4)

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Contribution from the Department of Chemistry, University of Kentucky,

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Abstract: Tetrakis(dimethylamino)diborane(4), $(Me_2N)_2B-B(NMe_2)_2$, reacts with four molar equivalents of pyrazole (= Hpz) to form the corresponding species $(pz)_2B-B(pz)_2$ as a dimer with a unique triply bridged pyrazabole structure but in mixture with polymeric product of the same elemental composition; and with excess of Hpz to form the adduct tetrakis(1-pyrazolyl)diborane(4)-bis(pyrazole), $(pz)_2B-B(pz)_2 \cdot 2Hpz$, which can be formulated as $H_2[(pz)_3B-B(pz)_3]$. This latter compound crystallizes in the triclinic system in space group $P\bar{1}$ (#2) with $\underline{a}$ = 13.945(2) Å, $\underline{b}$ = 18.392(3) Å, $\underline{c}$ = 9.048(2) Å, $\underline{\alpha}$ = 109.92(2)°, $\underline{\beta}$ = 94.85(1)°, $\underline{\gamma}$ = 105.18(1)°, Z = 4 at 296(2) K. The salt $K_2[(pz)_3B-B(pz)_3]$ is obtained on reaction of $(Me_2N)_2B-B(NMe_2)_2$ with two equivalents of Kpz and excess Hpz. This potassium salt reacts with π-allyl-palladium chloride dimers (allyl = CH_2CHCH_2 or $CH_2CCH_3CH_2$) to give $(\eta^3$-allyl)Pd$(\mu$-pz$)_2$(pz)B-B(pz)$(\mu$-pz$)_2$Pd$(\eta^3$-allyl) complexes, thus establishing the $[(pz)_3B-B(pz)_3]^{2-}$ ion as a novel bis-polydentate ligand. In solution the Pd$(\mu$-pz$)_2$B(pz) moieties are fluxional and only one set of ^{1}H NMR signals is observed for the pz groups, even at low temperatures. The formulation involving two bridging and one terminal pz groups at each boron site is, however, supported by X-ray diffraction data. The complex $(\eta^3$-CH_2CHCH_2)Pd$(\mu$-pz$)_2$(pz)B-B(pz)$(\mu$-pz$)_2$Pd$(\eta^3$-CH_2CHCH_2) crystallizes in the monoclinic system either in space group P2/c (#13) or Pc (#7) with $\underline{a}$ = 18.864(4) Å, $\underline{b}$ = 9.925(3) Å, $\underline{c}$ = 16.626(4) Å, $\underline{\beta}$ = 115.11(2)°, and Z = 4 at 296(2) K.

Introduction

$\underline{N}$-Bonded borane(3) derivatives of pyrazole (which normally exist in the dimeric pyrazabole structure containing a chemically stable B_2N_4 heterocycle with four-coordinate boron, e.g., $R_2B(\mu\text{-pz})_2BR_2$ where Hpz = pyrazole) and of the tetrahydroborate ion have been known for about 20 years. The pyrazaboles have been studied in limited detail, but poly(1-pyrazolyl)borate anions, $[R_{4-n}B(pz)_n]^-$ (n = 2-4, R = non-coordinating substituent), have been used extensively as chelating ligands in transition metal chemistry.[1]

The present study was based on the assumption that a neutral $(pz)_2B-B(pz)_2$ species would likely exist in a polymeric structure. Therefore, it should contain the bridging $B(\mu\text{-pz})_2B$ units typical for pyrazaboles but also terminal B-bonded pz groups and thus would be related to B-poly(1-pyrazolyl)pyrazaboles. Furthermore, a $[(pz)_3B-B(pz)_3]^{2-}$ ion should be similar to a $[RB(pz)_3]^-$ ion but for the fact that the former has two polydentate sites. These possibilities should provide for interesting variations as compared to the chemistry of B-(1-pyrazolyl)pyrazaboles and poly(1-pyrazolyl)borates, respectively.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were obtained on a Mel-Temp block.

NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for ^1H NMR, external $Et_2O\cdot BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, h = heptet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling

constants $\underline{J}$ are given in Hz. Mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer.

$[(pz)_2B-B(pz)]_n$. A mixture of 2.97 g (15 mmol) of tetrakis(dimethyl-amino)diborane(4),[2] 4.22 g (62 mmol) of pyrazole, and 50 mL of benzene was refluxed with stirring for several h. (If formed, a very small amount of insoluble material was filtered off; it was identified as $H_2[(pz)_3B-B(pz)_3]$, see below.) On cooling of the reaction mixture to room temperature, a colorless precipitate (2-2.5 g) was formed and collected. Concentration of the filtrate gave additional product for a total yield of about 3.6 g (84%) of dried (for 24 h under vacuum over paraffin wax) crude product. A ^{1}H NMR spectrum of this material showed traces of methyl signals and a strong benzene signal as impurities. These disappeared on heating of the material in an oil-bath (80 °C for 24 h, then 16 h at 200 °C) under high vacuum (10^{-3} torr). Some pyrazole sublimed off and the residue analyzed for the expected composition $C_6H_6BN_4$ but exhibited a complex ^{1}H NMR spectrum.

$[(pz)_2B-B(pz)_2]_2$ (1a) was isolated from this mixture by sublimation (24 h at 260 °C bath temperature at 10^{-4} torr). The pure dimer (30-50% of the crude product) has a mp 298-300 °C decomposition.

NMR data (solutin in $CDCl_3$): δ (^{1}H) 7.74 (1 H, d, $\underline{J}$ = 1.6), 7.53 (1 H, d, $\underline{J}$ = 2.3), 7.06 (2 H, d, $\underline{J}$ = 2.4), 6.34 (1 H, unsym t = two overlapping d in high-resolution spectrum), 6.04 (1 H, t, $\underline{J}$ = 2.4); δ ([11]B) 2.2 (s, $\underline{h}_{1/2}$ = 570 Hz). Selective decoupling experiments showed that the sets δ (^{1}H) 7.06/6.04 and 7.74/7.53/6.34, respectively, belong to individual (bridging and terminal) pz groups.

The 14 eV mass spectrum of the material exhibited only one major ion cluster near $\underline{m/z}$ 579 (clearly containing 4 B atoms). In the 70 eV spectrum, major ion clusters were observed in the $\underline{m/z}$ 579, 301, 289, 223, and 79

3

regions, and additional clusters were found near m/z 511, 445/444, 435, 377, 368, and 195.

$[(pz)_2B-B(pz)_2]_n$, $n > 2$ (**1b**), remained as residue after the above sublimation. This material changed color to a pale brown on heating to about 300 °C and began to decompose leaving an intractible material which was not further characterized. Part of the original sublimation residue was readily soluble in chloroform. The ^{1}H NMR spectrum of this material showed bridging $[\delta(^1H)$ 7.58 (2 H, d, J = 2.0)/6.34 (1 H, t, J = 2.0)] and two different types of terminal $[\delta(^1H)$ 7.60 (1 H, d, J = 1.6)/6.96 (1 H, d, J = 2.2)/6.31 (1 H, unsymmetrical t = two overlapping d) and 7.52 (1 H, d, J = 2.4)/7.19 (1 H, d, J = 2.4)/6.10 (1 H, unsymmetrical t = two overlapping d)] pz groups, identified by selective decoupling experiments. The ^{11}B NMR spectrum exhibited an extremely broad ($h_{1/2}$ ca. 1500 Hz) and unsymmetrical signal with a maximum near 1.4 ppm. These data suggest a species with n = 3. The insoluble part was not further investigated.

$H_2[(pz)_3B-B(pz)_3]$. A solution of 2.97 g (15 mmol) of tetrakis(dimethylamino)diborane(4)[2] in 10 mL of toluene was added dropwise with stirring to a refluxing solution of 6.8 g (0.1 mol) of pyrazole in 50 mL of toluene. The mixture was refluxed for 6 h. After cooling to room temperature, the colorless precipitate was collected, washed extensively with ether and dried under vacuum to yield 4.03 g (63%) of the crude product, mp 216-222 °C dec. A purified sample, mp 220-224 °C, was obtained by dissolving the crude product in methylene chloride and precipitation with hexane.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.59 (1 H, d, J = 1.9), 7.07 (1 H, d, J = 1.6), 6.18 (1 H, unsym t = two overlapping d, J = 1.8); $\delta(^{11}B)$ 1.8 (s, $h_{1/2}$ = 450 Hz).

4

Crystal and Molecular Structure of $H_2[(pz)_3B-B(pz)_3]$. The compound tetrakis(1-pyrazolyl)diborane(4)-bis(pyrazole), $C_{18}H_{20}N_{12}B_2$, crystallizes as colorless laths in the triclinic system with $\underline{a}$ = 13.945(2), $\underline{b}$ = 18.392(3), $\underline{c}$ = 9.048(2) A, $\underline{\alpha}$ = 102.92(2), $\underline{\beta}$ = 94.85(1), $\underline{\gamma}$ = 105.18(1)$^\circ$, and Z = 4 at 296(2) K. There are two full formula units in the asymmetric unit of the space group $P\bar{1}$ (#2; centrosymmetric choice confirmed by the sucessful refinement). All data with h ⩾ 0 and 2θ ⩽ 50° were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation and a graphite monochromator (7582 unique reflections). Data with 50° < 2θ < 55° were measured but were not included in the analysis since only 47 of 2306 reflections had I > $3\sigma(I)$. No correction was made for decomposition (ca. 1.6% overall), absorption (crystal size 0.16 x 0.25 x 0.38 mm; μ = 0.811 cm^{-1}), or extinction. The structure was solved using MULTAN77[3] after the overall temperature factor originally estimated by NORMAL was increased. Other programs and procedures utilized for crystal structure solution, refinement, and analysis have been described previously.[4] Refined values of the isotropic displacement parameters were used to distinguish between the N and C atoms in the 2 and 5 positions of the pyrazole rings; most of these assignments were later confirmed (see below). Hydrogen atoms attached to C atoms could be located in a difference Fourier map, but were placed in calculated positions [r(C-H) = 1.04 A; B_H 1.0 A^2 greater than B_{equ} for the attached C atom]. After refinement of this model to convergence (full-matrix least-squares; agreement factors R and R_w on F_o of 0.047 and 0.050) the positions of the four remaining H atoms could be inferred from the N···N distances. Within each fragment two such distances shorter than 2.63 A were found; all other N···N distances were greater than 2.83 A. Nitrogen atoms are not found so close together uniess they linked by a hydrogen bond. A difference map revealed four peaks with heights 0.30-0.32 e^- A^{-3}; all other

peaks had heights < 0.20 e$^-$ A^{-3}. The locations of three of the four peaks were consistent with the formation of H bonds [r(N-H) = 1.08-1.14 A; r(H$\cdots$N) = 1.51-1.57 A; <(N-H$\cdots$N) = 158-171°]. The fourth peak was located intermediate between two N atoms [r(N-H) = 1.30, 1.31 A; <(N-H-N) = 169°]. These four H atoms were included as fixed contributions after idealization [r(N-H)=1.00 A; B_H 1.0 A^2 greater than B_{equ} for the attached N atom]. At convergence (maximum shift/error = 0.0) the factors R and R_w on F_o dropped to 0.044 and 0.046 for 577 variables and the 3199 reflections having F_o^2 > $3\sigma(F_o^2)$. The error in an observation of unit weight is 2.01. The deepest troughs in a final difference Fourier map have heights ca. -0.24 e A^{-3} and are located at the centers of the pyrazole rings. The biggest peak has height 0.20 e$^-$ A^{-3} and is located near N(24), which is not involved in any H bond. Several other observations suggested that the C and N atoms in this ring may not have been assigned correctly. The N(24)-C(34) bond length is about 0.03 A too long and the C(35)-C(36) bond about 0.03 A too short. The B values for N(24) and C(36) are a little high and low, respectively. The orientation of the N-N bond relative to the B-B bond is reversed in this ring relative to what is found for the other three analogous rings; that is, the torsion angle N(24)-N(23)-B(4)-B(3) is much less than 90° while the torsion angles N(6)-N(5)-B(1)-B(2), N(12)-N(11)-B(2)-B(1), and N(18)-N(17)-B(3)-B(4) are all much greater than 90°. We tried re-refining the structure after reversing the N(24) and C(36) assignments and relocating H(36). The agreement factors at convergence were a little higher than before (0.046 and 0.048; observation in a reflection of unit weight = 2.11), and the bond length discrepancies increased from about 0.03 to 0.05 A. We strongly suspect that this ring adopts two orientations, but did not consider further refinement worthwhile. The atomic coordinates given in Table I correspond to the major orientation.

6

Table I

$K_2[(pz)_3B-B(pz)_3]$. Freshly prepared Kpz (11.75 g, 120 mmol) was added in portions to a stirred solution of 11.90 g (60 mmol) of $(Me_2N)_2B-B(NMe_2)_2$ in 75 mL of toluene. Pyrazole (20.4 g, 300 mmol) was then added in portions and the mixture was refluxed with stirring for 20 h. After cooling to room temperature, the solid material was collected, washed with toluene, then with copious amounts of ether, and finally with some absolute alcohol. The resultant crude product, mp 366-370 ^{o}C dec, was obtained in essentially quantitative yield and was used without further purification (although elemental analysis data suggest the material to be slightly impure; traces of adhering Hpz can be sublimed off under vacuum). NMR data were not obtained due to solubility problems.

$(\eta^3-CH_2CCH_3CH_2)Pd(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta CH_2CCH_3CH_2)$. A mixture of 1.34 g (2.67 mmol) of crude $K_2[(pz)_3B-B(pz)_3]$ (see above), 1.05 g (2.67 mmol) of $[(\eta^3-CH_2CCH_3CH_2)PdCl]_2$, and 50 mL of CH_2Cl_2 was stirred for 30 min to give a colorless solution containing a colorless precipitate. The latter was filtered off (0.40 g of KCl) and the clear filtrate was evaporated under vacuum to give 1.95 g of a faintly yellow solid. The latter was recrystallized from CH_2Cl_2 to yield 0.70 g of colorless product, decomposing near 170 ^{o}C. Anal. $(C_{26}H_{32}B_2N_{12}Pd_2)$ C, H, B, N, Pd.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ 7.51 (6 H, d, $\underline{J}$ = 1.8), 6.01 (3 H, unsym t = 2 overlapping d, $\underline{J}$ ca. 2), 3.44 (2 H, s), 2.49 (2 H, s), 1.86 (3 H, s); $\delta(^{11}B)$ 2.4 ($\underline{h}_{1/2}$ = 600 Hz). In low-temperature spectra, all ^1H NMR signals began to broaden near -25 ^{o}C but no signal separation was observed at temperatures as low as -50 ^{o}C.

$(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)$ was prepared in similar fashion as the preceding compound as a colorless solid decomposing near 170 $^\circ$C (86% yield). Anal. ($\text{C}_{24}\text{H}_{28}\text{B}_2\text{N}_{12}\text{Pd}_2$) C, H, B, N, Pd.

NMR data (solution in CDCl_3): $\delta(^1\text{H})$ 7.49 (6 H, d, $\underline{J}$ = 1.8, of d, $\underline{J}$ = 0.6), 6.04 (3 H, unsym t; resolution enhanced: 2 overlapping d, $\underline{J}$ = 2.3 each), 5.25 (1 H, h), 3.66 (2 H, d, $\underline{J}$ = 6.8), 2.46 (2 H, d, $\underline{J}$ = 12.4); $\delta(^{11}\text{B})$ 2.0 (s, $\underline{h}_{1/2}$ = 600 Hz). The ^1H NMR signals broaden on lowering of the temperature but no separation of signals was observed at -50 $^\circ$C.

The mass spectrum of the compound exhibits a very weak parent ion cluster in the $\underline{m}/\underline{z}$ 718 region; ready loss of one allyl or one pz group from the parent was also observed.

Crystal and Molecular Structure of $(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Pd}(\mu\text{-pz})_2(\text{pz})\text{B-B}(\text{pz})(\mu\text{-pz})_2\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)$. The compound crystallizes as colorless chunks and prisms in the monoclinic system with $\underline{a}$ = 18.864(4), $\underline{b}$ = 9.925(3), $\underline{c}$ = 16.626(4) Å, $\underline{\beta}$ = 115.11(2)$^\circ$, and Z = 4 at 296(2) K. The systematic absences, h0ℓ, ℓ = 2n+1, correspond either to the centrosymmetric space group P2/c (#13) or the non-centrosymmetric space group Pc (#7). All data with h,k $\geqslant$ 0 and 2θ $\leqslant$ 55° were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation and a graphite monochromator (6449 unique reflections). No correction was made for change of intensity with X-ray exposure (ca. +0.5% overall). An empirical correction was made for absorption (crystal size 0.16 x 0.25 x 0.38 mm; μ = 12.96 cm^{-1}); correction factors ranged from 1.20-1.49 and averaged 1.37. The structure was solved easily in the space group P2/c; the Pd atoms were located from a Patterson map and the program DIRDIF[5] revealed the positions of all the other atoms. Peak heights and refined values of the isotropic displacement parameters were used to distinguish between the N and C atoms in the 2 and 5 positions of the two pyrazole rings that are not coordinated to Pd atoms.

Problems with the structure became apparent during anisotropic refinement. Atomic $\underline{U}$ tensors for the allyl C atoms attached to the Pd(2) atoms are just barely positive definite. Bond lengths in the ring composed of atoms N(5), N(6), C(7), C(8), and C(9) and in the allyl group composed of atoms C(22), C(23), and C(24) deviate markedly from standard values. Estimated standard deviations on all bond lengths and angles are larger than expected. The weighted agreement factors for reflections having h = 0 or k = 0 are significantly higher than average; the agreement is especially poor for reflections having h = 0 and either k = 2n or ℓ = 2n+1. In a "final" difference Fourier map there is a rather large peak (1.5 e^- A^{-3}) within 2.1 A of C(14) and 1.5 A from the calculated position of H(14). There were, however, no unreasonable intermolecular contacts.

We considered the possibility that this structure could be described better in the non-centrosymmetric group Pc. The morphology of many of the crystals can be imagined to lack an inversion center. According to the programmers who wrote DIRDIF, the distribution of reflection intensities may correspond to a non-centrosymmetric atomic distribution. We have the impression that Pc is a more common space group than P2/c. An initial structure solution in the group Pc was obtained from DIRDIF; isotropic refinements, however, yielded unreasonable bond lengths and angles, even when the C_3N_2 rings and C_3 allyl groups were treated as rigid bodies. Most of the structure probably conforms well to the symmetry of the group P2/c, but the allyl groups at the ends of the molecules probably do not. The C_3N_2 ring containing the atoms N(5) and N(6), which is not coordinated to any Pd atom, may also adopt two slightly different positions. It should be noted that all 57 reflections included in the final refinement that have $(F_o - F_c) > 10\sigma(F_o)$, also have $F_o > F_c$, often by a substantial amount. This pattern suggests that

significant localized electron density is missing from the model. In any event, any deviations of the structure from inversion symmetry are not large enough to allow sucessful refinement in the lower symmetry group. The distances between superimposed atoms range from about 0.1 to 0.4 A if an inversion center is added to the Pc model.

In the final refinement the H atoms of the C_3N_2 rings were placed in calculated positions [r(C-H) = 1.00 Å; B_H 1.0 Å^2 greater than B_{equ} for the attached C atom]; the H atoms of the allyl groups were not included in the model. At convergence (maximum shift/error = 0.09) the agreement factors R and R_w on F_0 are 0.056 and 0.077 for 361 variables and the 3693 reflections having $F_0^2 \geqslant 3\sigma(F_0^2)$. The values of R and R_w on I for all 6449 reflections are 0.109 and 0.138 (negative intensities set to zero). None of the 2756 reflections omitted from the refinement cycles has $|I_0 - I_c| > 3\sigma(I)$. The error in an observation of unit weight is 3.48. A final difference Fourier map has the peak described above, and a set of peaks (ca. 0.7 e$^-$ A^{-3}) and troughs (ca. -1.1 e$^-$ A^{-3}) in the regions of the Pd atoms and allyl groups.

Positional parameters for the atoms of $(\eta^3\text{-}CH_2CHCH_2)Pd(\mu\text{-}pz)_2(pz)B\text{-}B(pz)(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CHCH_2)$ are given in Table II.

Table II

Results

$(pz)_2B\text{-}B(pz)_2$. Reaction of four molar equivalents of pyrazole (= Hpz) with tetrakis(dimethylamino)diborane(4), $(Me_2N)_2B\text{-}B(NMe_2)_2$, proceeds in a simple transamination reaction. However, solvent (benzene) adheres strongly to the product and can only be removed by prolonged heating of the material under vacuum. After such treatment the product analyzes as $(pz)_2B\text{-}B(pz)_2$ and the ^1H

NMR spectrum of the crude product exhibits only signals for pz groups and in the correct ratio of 2:1 for H(3,5) (7.8 to 7.0 ppm region) and H(4) (6.4 to 6.0 ppm region) of pz groups. The spectrum is, however, quite complex although it is dominated by two equally abundant sets for a bridging $[\delta(^{1}H)$ 7.06(2 H)/6.04(1 H)] and a terminal $[\delta(^{1}H)$ 7.74(1 H)/7.53(1 H)/6.34(1 H)] pz group. The abundance of these signals varied somewhat (30-50% of the total) in accordance with the mode of combining the reactants, the duration of the reflux period, and the temperature control during solvent removal.

The cited sets of ^{1}H NMR signals belong to a dimeric species $[(pz)_2B-B(pz)_2]_2$ (1a), which was isolated from the crude product by sublimation. The additional ^{1}H NMR signals are due to polymeric species of the general structure 1b.
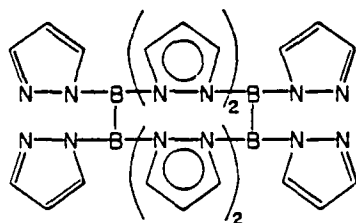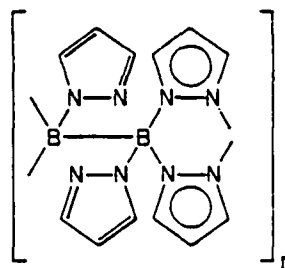
1a   1b

The sublimation residue (1b) contained a fraction which was soluble in chloroform. The ^{1}H NMR spectrum of this portion showed only one type of bridging but two different but equally abundant types of terminal pz groups in 1:1 ratio (terminal:bridging). This would seem to be in best agreement with 1b and n = 3, likely to be a linear polymer $(pz)_2B-B(pz)(\mu-pz)_2B(pz)-B(pz)(\mu-pz)_2B(pz)-B(pz)_2$. The chloroform-insoluble part (which is partially soluble in benzene) is then a mixture of 1b with n being variable but >3.

$H_2[(pz)_3B-B(pz)_3]$. Reaction of $(Me_2N)_2B-B(NMe_2)_2$ with excess Hpz leads to the formation of the complex $(pz)_2B-B(pz)_2 \cdot 2Hpz$ which may also be formulated as $H_2[(pz)_3B-B(pz)_3]$. The two acidic protons are generally not observed in the ^1H NMR spectrum but were identified in an X-ray structure determination of the compound; they are also clearly evident in the IR spectrum of the compound ($\nu(NH) = 3125$ cm^{-1}).

The crystal and molecular structures of the species were determined by single crystal X-ray diffraction. Selected bond length and bond angle data are given in Table III together with data for $(\eta^3-CH_2CHCH_2)Pd(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta^3-CH_2CHCH_2)$ (see below). ORTEP plots of the two independent molecules of the asymmetric unit of $H_2[(pz)_3B-B(pz)_3]$ are shown in Figure 1; a stereoscopic view is given in Figure 2.

Table III

Figure 1

Figure 2

In the solid state, the two acidic protons of $H_2[(pz)_3B-B(pz)_3]$ are localized between two pz groups bonded to two adjacent boron atoms. The B-N bonds of those pz groups (1.579(10) Å) are a little longer than are those for the pz groups which are not involved in hydrogen bonding (1.544(5) Å). All B-N bonds are considerably longer than those reported for B,B'-bis(1,2-dimethyl-1,3,2-diazaborilidin-2-yl), a diborane(4) derivative containing B-N bonds but trigonal boron.[6] The B-B bond distances (with an average value of 1.767(3) Å) are similar to but much more precise than those of the two other diborane(4) derivatives containing four-coordinate boron that are listed in the January 1987 Cambridge Structural Database,[7] i.e., $B_2H_4 \cdot 2P(C_6H_5)_3$[8]

12

(1.76(2) A) and $B_2Cl_4 \cdot 2N(CH_3)_3$[9] (1.72 A; no esd available). The B-B distance in $H_2[(pz)_3B-B(pz)_3$ appears to be longer than those of diborane(4) derivatives containing trigonal boron, which average 1.70 A.[6,10,11] Bond distances within the pz skeletons fall in the normal range observed in similar molecules, e.g., $(pz)_2B(\mu-pz)_2B(pz)_2$.[12]

$(\eta^3$-allyl)Pd$(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta^3$-allyl). The salt $K_2[(pz)_3B-B(pz)_3]$ was obtained on reaction of $(Me_2N)_2B-B(NMe_2)_2$ with two molar equivalents of Kpz and an excess of Hpz. No NMR data were obtained for the salt (due to solubility problems) and analytical data suggested the material to be slightly impure. Nevertheless, the crude material can be used for reactions with metal complexes such as $(\eta^3$-allyl)palladium chloride dimers to yield species of the type $(\eta^3$-allyl)Pd$(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta^3$-allyl) (allyl = CH_2CHCH_2 or $CH_2CCH_3CH_2$).

Even at low temperatures only one set of (two) pz signals is observed in the ^{1}H NMR spectra of these latter complexes, thus implying spectroscopic identity for the pz groups. This observation is common for some poly(1-pyrazolyl)borate complexes and has been ascribed to exchange processes of bridging and terminal pz groups that is fast on the NMR time scale. Frequently, this fluxional behavior is slowed down on lowering of the temperature, but this was not the case for the present Pd complexes. However, the above formulation of the complexes is clearly supported by a single crystal X-ray structure determination.

Bond distances and angles for $(\eta^3$-CH$_2$CHCH$_2$)Pd$(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2$Pd-$(\eta^3$-CH$_2$CHCH$_2)$ have been given in Table III. An ORTEP plot of the molecule is shown in Figure 3. Although precision of the structure determination was

Figure 3

13

limited by space group problems, the data clearly establish that, in the solid state, only two of the three pz groups attached to each B atom bond to the Pd. In general, bond distances are quite similar to those found for $H_2[(pz)_3B-B(pz)_3]$ (see above).

Discussion

When tris(dimethylamino)borane, $(Me_2N)_3B$, and pyrazole, Hpz, are combined in solution, the primary product is the complex $Me_2HN\cdot B(pz)_3$. The reaction is reasonably independent of the stoichiometry of the reagents and the temperature. At room temperature, the (N)H proton is not localized and the species is best formulated as $H[Me_2NB(pz)_3]$. Even in the presence of a large excess of Hpz, the remaining dimethylamine is not displaced to form $Hpz\cdot B(pz)_3$ = $H[B(pz)_4]$. Rather, under thermolytic conditions and in the presence of excess Hpz, the pyrazabole $(pz)_2B(\mu-pz)_2B(pz)_2$ is the ultimate product.[13]

The reaction of Hpz with tetrakis(dimethylamino)diborane(4), $(Me_2N)_2B-B(NMe_2)_2$, with Hpz is distinctly different. Even under mild conditions and employing a 4:1 stoichiometry of reactants, all four dimethylamino groups are readily displaced to form the pyrazabole $[(pz)_2B-B(pz)_2]_2$ (1a) and a polymeric species (1b) of the same composition; and in the presence of excess Hpz, the species $(pz)_2B-B(pz)_2\cdot 2Hpz$ = $H_2[(pz)_3B-B(pz)_3]$ is formed. These differences in chemical behavior clearly reflect an effect of the replacement of one Me_2N group of the borane(3) derivative $(Me_2N)_3B$ by $(Me_2N)_2B$ in the diborane(4) derivative $(Me_2N)_2B-B(NMe_2)_2$.

The species $[(pz)_2B-B(pz)_2]_2$ is an unusual pyrazabole. Its cage-like central $B_2(\mu-pz)_4B_2$ unit seems to be responsible for the fact that benzene (and other solvents) adheres strongly to the molecule. This feature may have some practical implications and needs to be explored in more detail.

14

Futhermore, the compound may be viewed as a triply bridged pyrazabole, i.e., as a species of the type $RB(\mu-pz)_2(\mu-X)BR$ where the two boron atoms of a pyrazabole skeleton $B(\mu-pz)_2B$ are linked by an additional moiety, i.e., X = $BR(\mu-pz)_2BR$ with R = pz. Only two other such species have previously been described, namely $RB(\mu-pz)_2(\mu-X)BR$ with X = OBRO and R = C_2H_5 or C_6H_5.[14] It may well be that other such triply bridged pyrazaboles exist and a search for the synthesis of such additional species with various X bridges is currently under way.

Similarly, the ion $[(pz)_3B-B(pz)_3]^{2-}$ acts like a typical poly(1-pyrazolyl)borate and may best be compared to the $[RB(pz)_3]^-$ ion (R = non-coordinating substituent) but for the fact that the former is bis(polydentate) and a dianion. Hence, whereas $[RB(pz)_3]^-$ forms monometallic complexes such as $RB(pz)_3ML$ (M = metal, L = other ligand(s)), the ion $[(pz)_3B-B(pz)_3]^{2-}$ forms bimetallic analogs, i.e., $LM(pz)_3B-B(pz)_3ML$. This event opens additional opportunities for the syntheses of novel polynuclear chain-type species containing boron and metal centers similar to those described recently.[15] Moveover, since the $[RB(pz)_3]^-$ ion can also act as tridentate ligand,[1] the $[(pz)_3B-B(pz)_3]^{2-}$ should behave in analogous fashion to give compact bimetallic complexes, possibly even containing two different metals in the same molecule, or macromolecular materials of the general composition $[(pz)_3B-B(pz)_3M]_n$.

Supplementary Material Available: Complete listing of bond lengths and angles, anisotropic displacement parameters, hydrogen-atom coordinates, and

final observed and calculated structure factor tables for $H_2[(pz)_3B-B(pz)_3]$ and for $(\eta^3-CH_2CHCH_2)Pd(\mu-pz)_2(pz)B-B(pz)(\mu-pz)Pd(\eta^3-CH_2CHCH_2)$ (55 pages). Ordering information is given on any current masthead page.

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17

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CAPTIONS FOR FIGURES

Figure 1. Perspective view of the two independent molecules of $H_2[(pz)_3B-B(pz)_3]$. In this and the other figures the shapes of the ellipsoids for the non-hydrogen atoms correspond to 50% probability contours of atomic displacement. The atom numbering in this compound and in $(\eta^3-CH_2CHCH_2)Pd(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta^3-CH_2CHCH_2)$ is defined by the numbers shown on the drawings by the information that the atoms within the pz rings are numbered sequentially $N(2n-1)$, $N(2n)$, $C(3n-2)$, $C(3n-1)$, $C(3n)$; the atoms $N(2n-1)$ participate in $\beta-N$ bonds.

Figure 2. Stereoscopic view of the two independent molecules of $H_2[(pz)_3B-B(pz)_3]$.

Figure 3. Perspective view of a molecule of $(\eta^3-CH_2CHCH_2)Pd(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta^3-CH_2CHCH_2)$ (see also caption to Figure 1).

Table I. Positional Parameters and Equivalent B Values for the Atoms of the Two Independent Molecules of Tetrakis(1-pyrazolyl)diborane(4)-Bis(pyrazole), $H_2[(pz)_3B-B(pz)_3]$.

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$B_{equ}(A^2)$
N(1)	0.2910(02)	0.67210(18)	0.1855(04)	3.1(1)
N(2)	0.2186(03)	0.70808(20)	0.1748(04)	4.3(1)
N(3)	0.4619(02)	0.65577(17)	0.1897(04)	2.8(1)
N(4)	0.5052(03)	0.68391(19)	0.3405(04)	3.5(1)
N(5)	0.3708(02)	0.66313(18)	-0.0557(04)	3.0(1)
N(6)	0.3120(03)	0.58768(20)	-0.1186(04)	4.3(1)
N(7)	0.3907(03)	0.84267(17)	0.0704(03)	3.0(1)
N(8)	0.2882(03)	0.82091(20)	0.0432(04)	4.1(1)
N(9)	0.4300(02)	0.83938(17)	0.3389(04)	3.0(1)
N(10)	0.4478(03)	0.80773(19)	0.4566(04)	3.9(1)
N(11)	0.5588(02)	0.82980(18)	0.1639(03)	2.8(1)
N(12)	0.6116(03)	0.90668(18)	0.2211(04)	3.6(1)
N(13)	-0.1258(02)	0.67040(19)	0.4524(04)	3.3(1)
N(14)	-0.1700(03)	0.70515(19)	0.3608(04)	4.0(1)
N(15)	-0.0417(03)	0.65693(20)	0.6947(04)	3.7(1)
N(16)	0.0579(03)	0.68777(22)	0.6940(04)	4.8(1)
N(17)	-0.2225(03)	0.65320(18)	0.6670(03)	3.0(1)
N(18)	-0.2673(03)	0.57648(19)	0.5913(04)	4.0(1)
N(19)	-0.1689(03)	0.83619(18)	0.6820(04)	3.4(1)
N(20)	-0.2251(03)	0.81750(20)	0.5400(04)	4.0(1)
N(21)	0.0010(03)	0.84018(19)	0.6175(04)	3.6(1)
N(22)	0.0804(03)	0.8129(02)	0.5886(04)	5.0(2)
N(23)	-0.0371(03)	0.82733(20)	0.8766(04)	3.3(1)
N(24)	-0.0546(03)	0.7827(02)	0.9788(04)	5.2(2)
C(1)	0.1413(04)	0.6759(03)	0.2377(06)	5.6(2)
C(2)	0.1631(04)	0.6172(03)	0.2922(06)	6.1(2)
C(3)	0.2577(04)	0.6167(03)	0.2574(05)	4.6(2)
C(4)	0.5646(03)	0.6410(03)	0.3676(05)	4.2(2)
C(5)	0.5606(04)	0.5844(02)	0.2351(05)	4.2(2)
C(6)	0.4946(03)	0.5956(02)	0.1268(05)	3.3(1)
C(7)	0.3157(04)	0.5756(03)	-0.2691(05)	4.3(2)
C(8)	0.3751(04)	0.6411(03)	-0.3028(05)	4.7(2)
C(9)	0.4089(03)	0.6952(02)	-0.1659(05)	3.4(1)
C(10)	0.2625(04)	0.8670(03)	-0.0376(06)	4.9(2)
C(11)	0.3462(04)	0.9190(03)	-0.0623(05)	4.7(2)
C(12)	0.4262(03)	0.9021(02)	0.0064(05)	3.8(2)
C(13)	0.4375(04)	0.8542(03)	0.5866(05)	4.7(2)
C(14)	0.4128(03)	0.9169(02)	0.5540(05)	4.3(2)
C(15)	0.4086(03)	0.90642(22)	0.3986(05)	3.5(1)
C(16)	0.7056(03)	0.9111(02)	0.1985(05)	3.9(2)
C(17)	0.7166(03)	0.8391(03)	0.1298(05)	4.1(2)
C(18)	0.6227(03)	0.7894(02)	0.1089(05)	3.8(2)
C(19)	-0.1766(04)	0.6677(03)	0.2151(05)	4.8(2)
C(20)	-0.1361(04)	0.6067(03)	0.2091(05)	5.2(2)

Table I, contd.

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$B_{equ}(A^2)$
C(21)	-0.1057(03)	0.6096(02)	0.3594(05)	4.2(2)
C(22)	0.1075(04)	0.6481(04)	0.7623(07)	6.6(2)
C(23)	0.0401(05)	0.5918(03)	0.8082(07)	6.7(2)
C(24)	-0.0538(04)	0.5986(03)	0.7645(06)	5.1(2)
C(25)	-0.3503(04)	0.5556(02)	0.6515(05)	4.1(2)
C(26)	-0.3619(04)	0.6163(03)	0.7635(05)	4.9(2)
C(27)	-0.2798(03)	0.6774(02)	0.7700(05)	4.0(2)
C(28)	-0.2911(04)	0.8580(03)	0.5525(06)	5.2(2)
C(29)	-0.2793(04)	0.9034(03)	0.7015(06)	5.2(2)
C(30)	-0.2010(04)	0.8881(02)	0.7796(05)	4.1(2)
C(31)	0.1422(04)	0.8627(04)	0.5280(06)	6.0(2)
C(32)	0.1047(04)	0.9225(03)	0.5163(06)	5.8(2)
C(33)	0.0153(04)	0.9069(03)	0.5726(05)	5.0(2)
C(34)	-0.0077(04)	0.8305(03)	1.1181(05)	4.7(2)
C(35)	0.0358(04)	0.9030(03)	1.0998(06)	5.2(2)
C(36)	0.0171(04)	0.9002(02)	0.9499(05)	3.9(2)
B(1)	0.3926(04)	0.6988(03)	0.1194(05)	2.7(2)
B(2)	0.4448(04)	0.8010(03)	0.1691(05)	2.7(2)
B(3)	-0.1198(04)	0.6961(03)	0.6325(05)	3.0(2)
B(4)	-0.0817(04)	0.7986(03)	0.7041(06)	3.4(2)

The equivalent displacement parameter is defined as $(4/3)Tr(\underline{\beta} \cdot \underline{G})$, where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

Table II. Positional Parameters and Equivalent B Values for the Atoms of $(\eta^3$-$CH_2CHCH_2)Pd(\mu$-$pz)_2(pz)B$-$B(pz)(\mu$-$pz)_2Pd(\eta^3$-$CH_2CHCH_2)$.

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$B_{equ}(\text{Å}^2)$
Pd(1)	0.16572(05)	0.13513(09)	0.21441(05)	3.10(3)
Pd(2)	0.38045(05)	-0.57653(09)	0.49023(06)	3.58(3)
N(1)	0.2168(04)	-0.0565(08)	0.3718(05)	2.6(3)
N(2)	0.1870(05)	0.0719(09)	0.3399(05)	3.4(3)
N(3)	0.2916(04)	-0.0769(08)	0.2752(05)	2.7(3)
N(4)	0.2674(05)	0.0364(08)	0.2262(05)	2.7(3)
N(5)	0.1591(04)	-0.1810(09)	0.2277(05)	2.9(3)
N(6)	0.1565(05)	-0.2129(10)	0.1508(05)	3.7(3)
N(7)	0.3581(05)	-0.2753(09)	0.4598(05)	3.1(3)
N(8)	0.4008(05)	-0.3727(09)	0.5160(06)	3.8(3)
N(9)	0.3064(05)	-0.4120(09)	0.3184(05)	3.1(3)
N(10)	0.3359(05)	-0.5350(09)	0.3566(06)	3.4(3)
N(11)	0.2246(05)	-0.3843(08)	0.4006(05)	2.8(3)
N(12)	0.2316(06)	-0.4007(10)	0.4827(06)	4.1(3)
C(1)	0.1732(07)	0.1320(12)	0.4058(08)	4.5(5)
C(2)	0.1892(06)	0.0445(12)	0.4745(07)	3.8(4)
C(3)	0.2169(06)	-0.0717(11)	0.4516(06)	3.3(3)
C(4)	0.3198(06)	0.0683(11)	0.1978(06)	3.0(3)
C(5)	0.3821(06)	-0.0216(12)	0.2302(07)	4.1(4)
C(6)	0.3612(06)	-0.1125(12)	0.2792(07)	3.6(4)
C(7)	0.0843(07)	-0.2330(14)	0.0978(08)	4.8(5)
C(8)	0.0350(06)	-0.2121(16)	0.1438(08)	5.7(5)
C(9)	0.0828(06)	-0.1783(14)	0.2229(08)	4.7(5)
C(10)	0.4592(07)	-0.3116(15)	0.5862(08)	5.1(5)
C(11)	0.4552(07)	-0.1720(12)	0.5746(07)	4.2(4)
C(12)	0.3916(06)	-0.1559(11)	0.4955(07)	3.7(4)
C(13)	0.3412(06)	-0.6122(11)	0.2913(08)	4.0(4)
C(14)	0.3112(07)	-0.5455(12)	0.2119(08)	4.2(4)
C(15)	0.2910(06)	-0.4155(12)	0.2312(06)	3.5(4)
C(16)	0.1692(07)	-0.4737(13)	0.4760(08)	4.3(5)
C(17)	0.1218(07)	-0.5003(12)	0.3922(10)	5.0(6)
C(18)	0.1571(07)	-0.4443(12)	0.3437(08)	4.8(5)
C(19)	0.0562(07)	0.2327(17)	0.1819(08)	6.4(6)
C(20)	0.0966(08)	0.2950(17)	0.1337(09)	6.8(6)
C(21)	0.1173(07)	0.2013(13)	0.0799(08)	4.6(4)
C(22)	0.4405(12)	-0.6551(19)	0.6224(10)	8.4(8)
C(23)	0.3791(12)	-0.7391(17)	0.5715(13)	8.3(9)
C(24)	0.3805(10)	-0.7907(13)	0.4871(12)	7.9(8)
B(1)	0.2393(06)	-0.1555(11)	0.3135(07)	2.2(3)
B(2)	0.2825(06)	-0.3082(13)	0.3734(07)	2.7(4)

The equivalent displacement parameter is defined as $(4/3)Tr(\underline{\beta}\cdot\underline{G})$, where $\beta_{ij} = 2\pi^2 a_i{}^* a_j{}^* U_{ij}$.

Table III. Selected Bond Lengths (Å) and Angles (deg) Including Average Values (Numbers in parentheses are estimated standard deviations. For the averages, the numbers in parentheses are the esd's of the means).

$H_2[(pz)_3B-B(pz)_3]$			$[(\eta^3-CH_2CHCH_2)Pd(\mu-pz)_2(pz)B-]_2$		
atoms		distance	atoms		distance
B(1)	B(2)	1.765(6)	B(1)	B(2)	1.807(16)
B(3)	B(4)	1.769(6)			
B(1)	N(1)	1.586(5)	B(1)	N(1)	1.560(12)
B(1)	N(3)	1.576(5)	B(1)	N(3)	1.587(12)
B(2)	N(7)	1.565(5)	B(2)	N(7)	1.570(13)
B(2)	N(9)	1.596(5)	B(2)	N(9)	1.566(14)
B(3)	N(13)	1.580(5)			
B(3)	N(15)	1.584(5)			
B(4)	N(19)	1.568(6)			
B(4)	N(21)	1.577(6)			
B(1)	N(5)	1.543(5)	B(1)	N(5)	1.598(12)
B(2)	N(11)	1.546(5)	B(2)	N(11)	1.545(13)
B(3)	N(17)	1.537(6)			
B(4)	N(23)	1.548(5)			
N(1)	N(2)	1.352(4)	N(1)	N(2)	1.403(11)
N(9)	N(10)	1.357(4)	N(3)	N(4)	1.350(10)
N(13)	N(14)	1.354(4)	N(7)	N(8)	1.348(11)
N(21)	N(22)	1.351(4)	N(9)	N(10)	1.380(11)
N(3)	N(4)	1.370(4)	N(5)	N(6)	1.298(10)
N(5)	N(6)	1.376(4)	N(11)	N(12)	1.326(10)
N(7)	N(8)	1.365(4)			
N(11)	N(12)	1.368(4)			
N(15)	N(16)	1.358(5)			
N(17)	N(18)	1.373(4)			
N(19)	N(20)	1.370(4)			
N(23)	N(24)	1.364(4)			
			Pd(1)	N(2)	2.049(8)
			Pd(1)	N(4)	2.088(8)
			Pd(2)	N(6)	2.070(10)
			Pd(2)	N(8)	2.056(9)
			Pd(1)	C(19)	2.133(10)
			Pd(1)	C(20)	2.130(12)

Table III. contd.

Pd(1)	C(21)	2.130(11)
Pd(2)	C(22)	2.147(13)
Pd(2)	C(23)	2.112(14)
Pd(2)	C(24)	2.126(14)
C(19)	C(20)	1.457(18)
C(20)	C(21)	1.454(17)
C(22)	C(23)	1.386(24)
C(23)	C(24)	1.506(22)

atoms			angle	atoms			angle
B(2)	B(1)	N(1)	112.6(3)	B(2)	B(1)	N(1)	111.3(7)
B(2)	B(1)	N(3)	113.0(3)	B(2)	B(1)	N(3)	114.9(7)
B(1)	B(2)	N(7)	113.4(3)	B(1)	B(2)	N(7)	110.6(8)
B(1)	B(2)	N(9)	111.5(3)	B(1)	B(2)	N(9)	113.8(8)
B(4)	B(3)	N(13)	112.1(3)				
B(4)	B(3)	N(15)	112.4(3)				
B(3)	B(4)	N(19)	113.2(4)				
B(3)	B(4)	N(21)	112.4(3)				
B(2)	B(1)	N(5)	112.7(3)	B(2)	B(1)	N(5)	113.2(8)
B(1)	B(2)	N(11)	115.1(3)	B(1)	B(2)	N(11)	111.2(8)
B(4)	B(3)	N(17)	115.8(3)				
B(3)	B(4)	N(23)	114.1(3)				
N(1)	B(1)	N(3)	103.1(3)	N(1)	B(1)	N(3)	108.5(8)
N(1)	B(1)	N(5)	107.5(3)	N(1)	B(1)	N(5)	104.5(7)
N(3)	B(1)	N(5)	107.3(3)	N(3)	B(1)	N(5)	103.6(7)
N(7)	B(2)	N(9)	102.3(3)	N(7)	B(2)	N(9)	107.2(8)
N(7)	B(2)	N(11)	107.6(3)	N(7)	B(2)	N(11)	108.3(8)
N(9)	B(2)	N(11)	105.8(3)	N(9)	B(2)	N(11)	105.3(9)
N(13)	B(3)	N(15)	103.8(3)				
N(13)	B(3)	N(17)	105.8(3)				
N(15)	B(3)	N(17)	106.0(3)				
N(19)	B(4)	N(21)	103.7(3)				
N(19)	B(4)	N(23)	106.6(3)				
N(21)	B(4)	N(23)	106.0(3)				
				N(2)	Pd(1)	N(4)	89.2(3)
				N(8)	Pd(2)	N(10)	89.0(3)
				C(19)	C(20)	C(21)	114.0(14)
				C(22)	C(23)	C(24)	115.6(18)

24

Table III, contd.

average values:

r(B-B)	1.767(3)	1.807(16)
r(B-N)	1.567(19)	1.571(19)
r(N-N)	1.363(9)	1.351(37)
r(N-C)	1.339(11)	1.348(31)
r(C-C)	1.372(11)	1.373(42)
r(Pd-N)		2.066(17)
r(Pd-C)		2.130(11)
r(C-C)$_{allyl}$		1.451(49)
<(B-B-N)	113.2(13)	112.5(17)
<(N-B-N)	105.5(18)	106.2(21)
<(N-N-C)	107.9(16)	107.8(13)
<(N-C-C)	109.4(12)	109.9(14)
<(C-C-C)	105.4(10)	104.6(11)
<(N-Pd-N)		89.1(1)
<(C-C-C)$_{allyl}$		114.8(11)
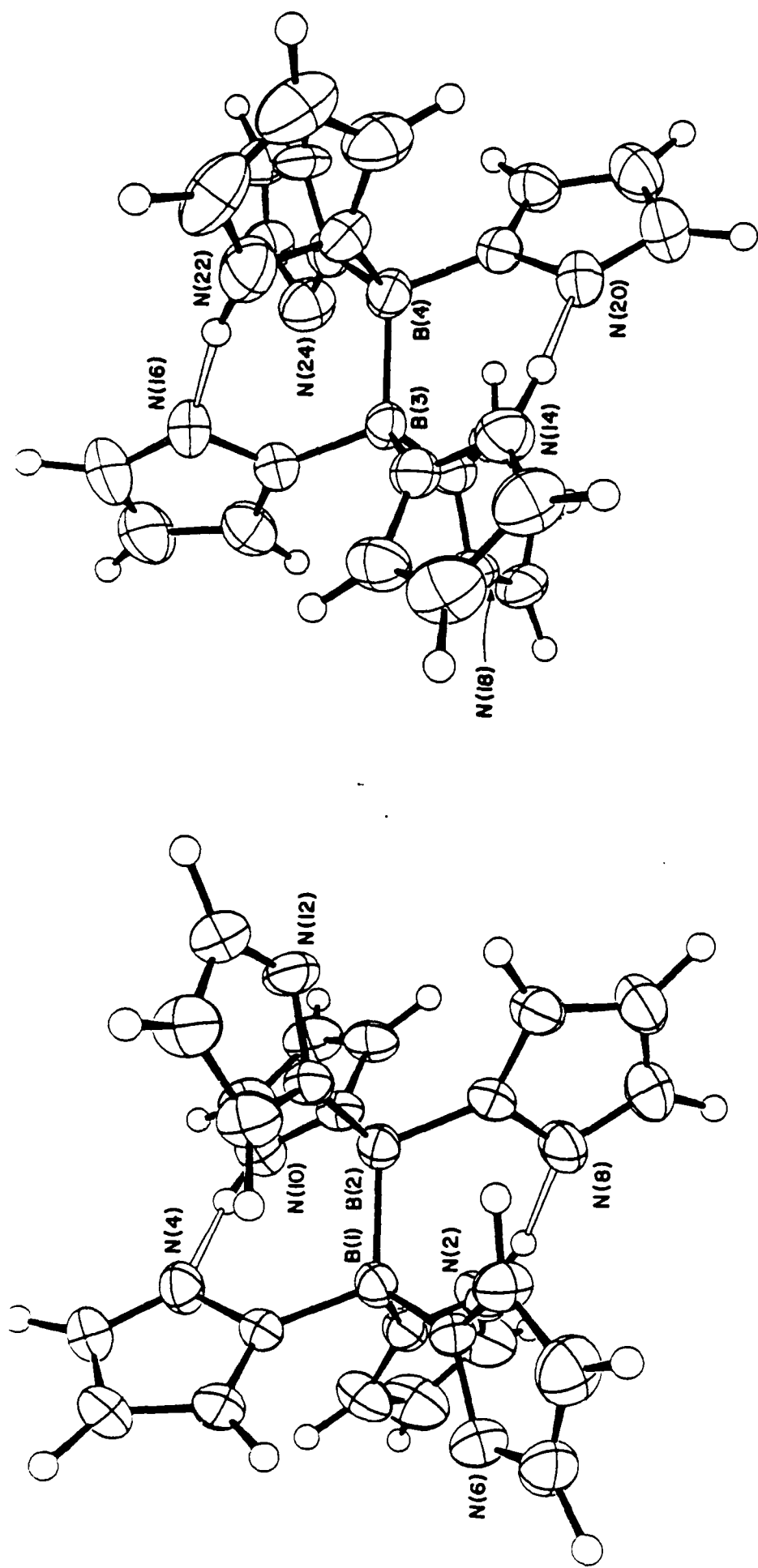
Figure 1. Perspective view of the two independent molecules of $H_2[(pz)_3B-B(pz)_3]$. In this and the other figures the shapes of the ellipsoids for the non-hydrogen atoms correspond to 50% probability contours of atomic displacement. The atom numbering in this compound and in $(\eta^3-CH_2CHCH_2)Pd(\mu-pz)_2(pz)B-B(pz)(\mu-pz)_2Pd(\eta^3-CH_2CHCH_2)$ is defined by the numbers shown on the drawings by the information that the atoms within the pz rings are numbered sequentially $N(2n-1)$, $N(2n)$, $C(3n-2)$, $C(3n-1)$, $C(3n)$; the atoms
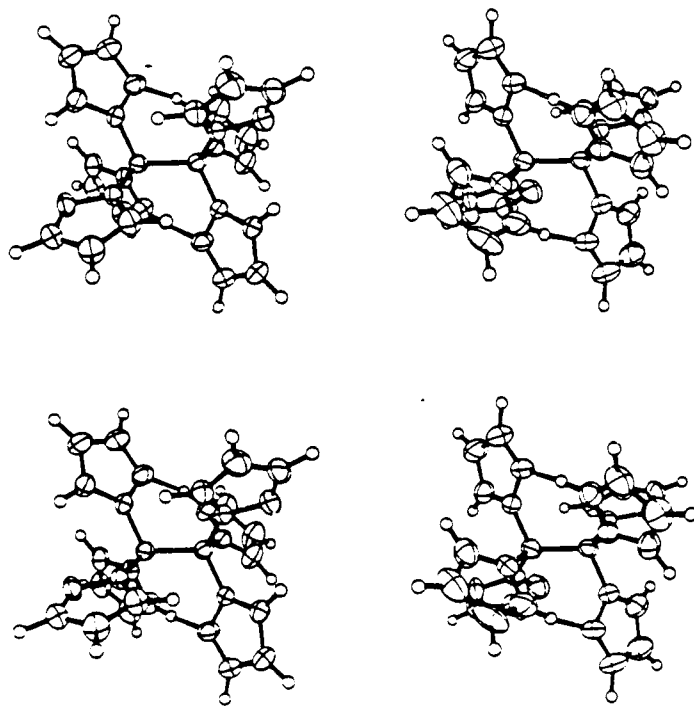
Figure 2. Stereoscopic view of the two independent molecules of $H_2[(pz)_3B-B(pz)_3]$.
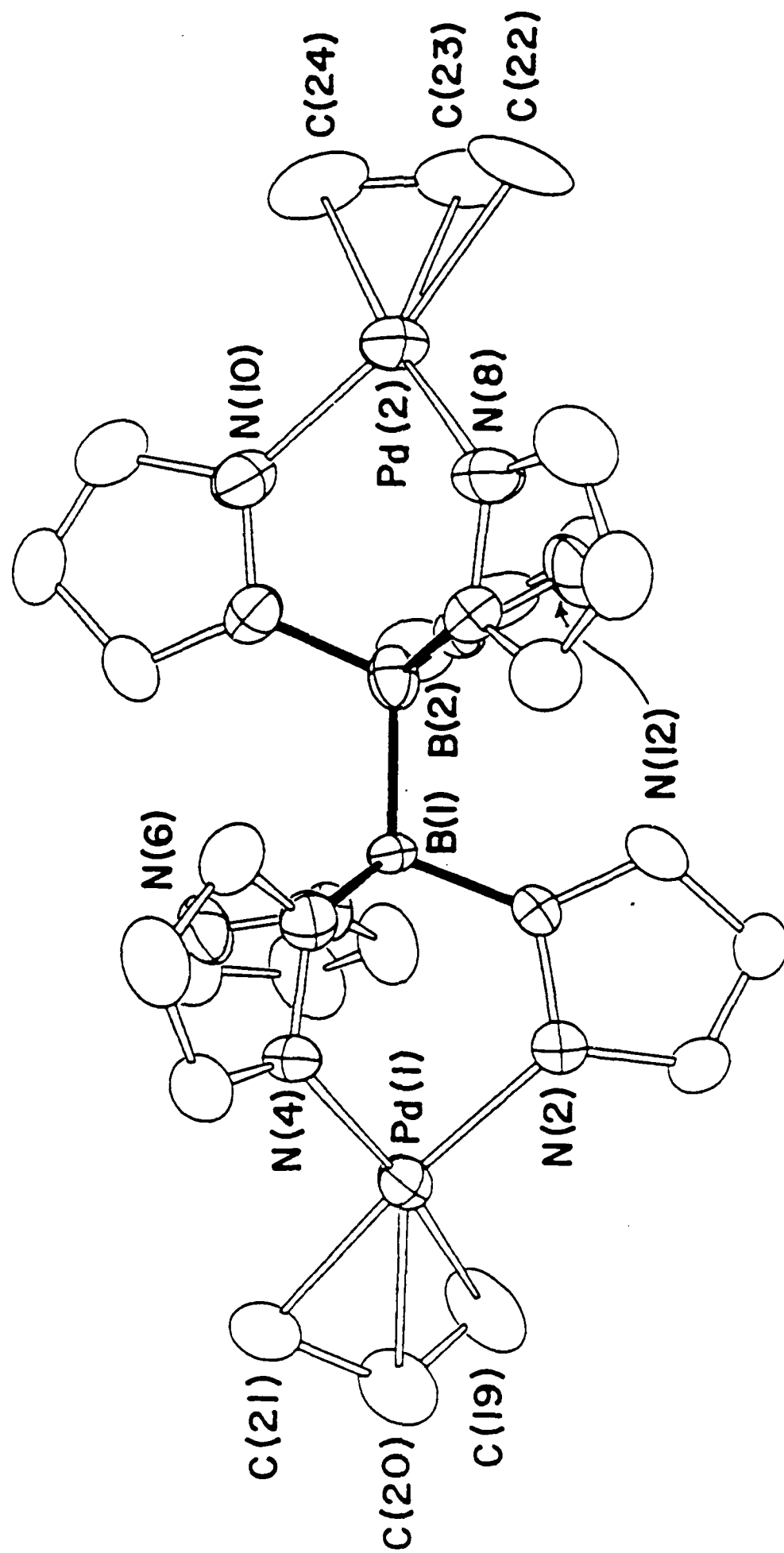
Figure 3. Perspective view of a molecule of $(\eta^3\text{-}CH_2CHCH_2)Pd(\mu\text{-}pz)_2(pz)B\text{-}B(pz)(\mu\text{-}pz)_2Pd(\eta^3\text{-}CH_2CHCH_2)$ (see also caption to Figure 1).

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